

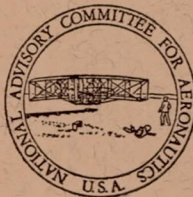
# NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

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REPORT 1290

## DEVELOPMENT OF CRAZE AND IMPACT RESISTANCE IN GLAZING PLASTICS BY MULTIAXIAL STRETCHING

By G. M. KLINE, I. WOLOCK, B. M. AXILROD, M. A. SHERMAN  
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**National Bureau of Standards**



# National Advisory Committee for Aeronautics

*Headquarters, 1512 H Street NW., Washington 25, D. C.*

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## REPORT 1290

### DEVELOPMENT OF CRAZE AND IMPACT RESISTANCE IN GLAZING PLASTICS BY MULTIAXIAL STRETCHING

By G. M. KLINE, I. WOLOCK, B. M. AXILROD, M. A. SHERMAN, D. A. GEORGE, and V. COHEN

#### SUMMARY

The loss of strength of cast polymethyl methacrylate plastic as a result of crazing is of considerable importance to the aircraft industry. Because of the critical need for basic information on the nature of crazing and the effects of various treatments and environmental conditions on its incidence and magnitude, an investigation of this phenomenon was undertaken.

In the course of this study of crazing the following factors were examined: (1) The effect of stress-solvent crazing on tensile strength of polymethyl methacrylate; (2) the critical stress and strain for onset of crazing at various temperatures; (3) the effect of molecular weight on crazing; and (4) the effect of multiaxial stretching on crazing of polymethyl methacrylate and other acrylic glazing materials.

It was found that moderate stress-solvent crazing of polymethyl methacrylate results in a loss in tensile strength of approximately 30 percent. Stress crazing develops at 80 to 95 percent of the tensile strength in the standard tensile test in the temperature range of 23° to 70° C. Craze resistance increases slightly with increasing molecular weight of the polymer. Multiaxial stretching of polymethyl methacrylate markedly increased its craze resistance. Material stretched 150 percent did not craze in short-time tensile tests and the crazing threshold was increased several fold in stress-solvent crazing tests. The strain at failure was increased several fold (up to 60 percent strain), thus imparting toughness to the stretched sheets. The orientation of the large molecules of this high-polymeric material transforms the amorphous, brittle cast sheets into laminar, tough products that are resistant to shattering under impact loads. Multiaxial stretching of other acrylic plastics, including polymethyl alpha-chloroacrylate, gave comparable results.

The improvement in the crazing resistance of acrylic plastic sheets produced by multiaxial stretching indicates that enclosures made from stretched sheets have crazing and strength properties superior to those of enclosures formed with little or no stretching. As an alternative to the use of prestretched material to achieve improved craze resistance and toughness in acrylic enclosures, there is the possibility of preparing a more highly stretched enclosure directly, such as by forming a larger and more deeply drawn enclosure than required and then using only the central portion of the formed piece. Either method would improve the craze resistance, particularly at the rim, where there

is likely to be stress concentration and where contact with solvents of adhesives used to seal the enclosure is quite likely; in a normally formed enclosure, the craze resistance is a minimum at the rim. The laminar structure of the stretched acrylic sheets also offers the possibility of obtaining resistance to shattering of pressurized acrylic canopies by shrapnel without the necessity of employing the heavier and more expensive acrylic laminate made with a safety-glass type of vinyl interlayer.

#### INTRODUCTION

Acrylic-plastic glazing has been used for many years in astrodomes, gun turrets, antenna covers, and other transparent curved enclosures in military aircraft. However, in spite of its good weathering and optical properties and the ease with which it can be formed into shapes with compound curvature, this material has several disadvantages such as low impact strength and craze cracking. Perhaps the most serious of these is its tendency to craze under stress, especially in the presence of organic solvents. This results not only in reduced visibility but also in lowered resistance to both steady and impact loads. Because of the critical need for basic information on the nature of crazing and the effects of various treatments and environmental conditions on its incidence and magnitude, an investigation of this phenomenon was conducted at the National Bureau of Standards under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

In the course of this study of crazing the following factors were examined: (1) The effect of stress-solvent crazing on tensile strength of polymethyl methacrylate; (2) the critical stress and strain for onset of crazing at various temperatures; (3) the effect of molecular weight on crazing; and (4) the effect of multiaxial stretching on crazing of polymethyl methacrylate and other acrylic glazing materials. It was found that craze-resistant glazing materials could be produced by the multiaxial-stretching process; furthermore, the orientation of the large molecules of these high polymeric materials transforms the amorphous, brittle, cast sheets into laminar, tough products that are resistant to shattering when subjected to gunfire.

The results obtained in the various phases of the investigation of crazing are presented in this report.



### EFFECT OF STRESS-SOLVENT CRAZING ON TENSILE STRENGTH OF POLYMETHYL METHACRYLATE

The loss of strength of tensile specimens of polymethyl methacrylate as a result of stress-solvent crazing at 23° C and 50-percent relative humidity was investigated (ref. 1). The materials tested were commercial cast polymethyl methacrylate sheets of both heat-resistant and general-purpose grades from each of two manufacturers. Most of the tests were made on samples 0.15 inch thick and covered with masking paper on one side only. The tensile specimens were artificially crazed by applying benzene to the central portion of the reduced section while under stress, as described in footnotes c and e of table I and in appendix A, and were subsequently broken. Specimens for controls were treated identically except that no benzene was applied. Among the factors studied were the effect of the masking paper on the crazing and the relative effect on tensile strength of a few large craze cracks compared with that of more numerous finer cracks. The coarse crazing was produced by applying a larger amount of benzene and a smaller stress than were used to create the fine crazing. The results are summarized in table I.

The crazing treatment that produced up to two coarse cracks per square millimeter with a crack length and depth of roughly 1 and 0.15 millimeter, respectively, caused a loss of strength that averaged approximately 35 percent for all materials. The loss in strength produced by the fine crazing averaged roughly 27 percent for all materials. It should be noted that, in order to produce this loss in strength, a higher stress was used in crazing the heat-resistant grade than was used in crazing the general-purpose material. This result agrees with the well-known fact that the threshold stress for

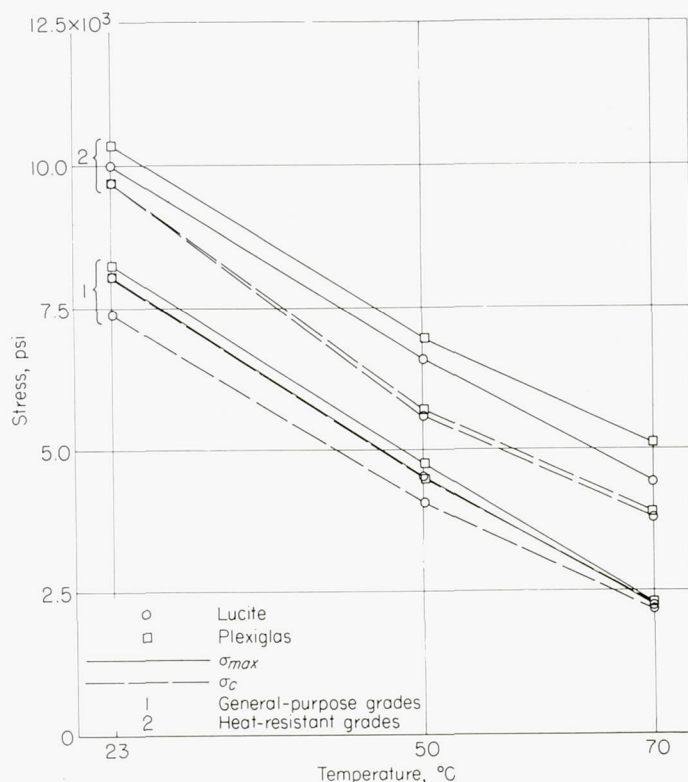


FIGURE 1.—Variation of tensile strength  $\sigma_{max}$  and stress at onset of crazing  $\sigma_c$  with temperature for acrylic plastics.

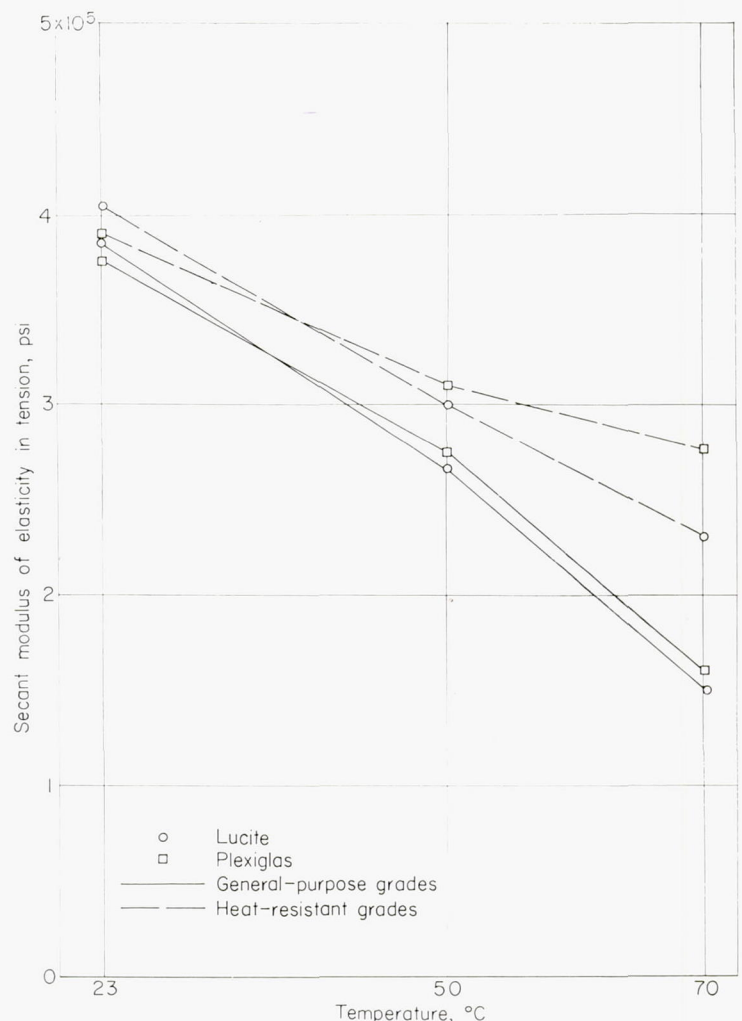


FIGURE 2.—Variation of tensile secant modulus of elasticity with temperature for acrylic plastics. Stress range is zero to about one-half of tensile strength.

solvent crazing is higher for the heat-resistant than for the general-purpose cast material. The masking paper had no statistically significant effect on the loss of strength resulting from crazing.

The crazed specimens were more variable than the controls, the coefficients of variation for tensile strength averaging about 15 and 5 percent, respectively, for all samples. In addition, although the crazing treatment was done in a controlled manner, there was a significant daily variation in treatment that contributed an additional 15 percent to the coefficient of variation for the crazed specimens. It was not found possible to predict the tensile strength of a crazed specimen from its appearance.

### STRESS AND STRAIN AT ONSET OF CRAZING OF POLYMETHYL METHACRYLATE AT VARIOUS TEMPERATURES

The stress and strain at the onset of crazing of polymethyl methacrylate were determined at 23°, 50°, and 70° C (ref. 2). The materials tested were commercial cast polymethyl methacrylate sheets of both general-purpose and heat-resistant grades. Most of the tests were made on samples 0.15 inch thick. The standard tensile test described in appendix A was used with the exception that when the strain gage was



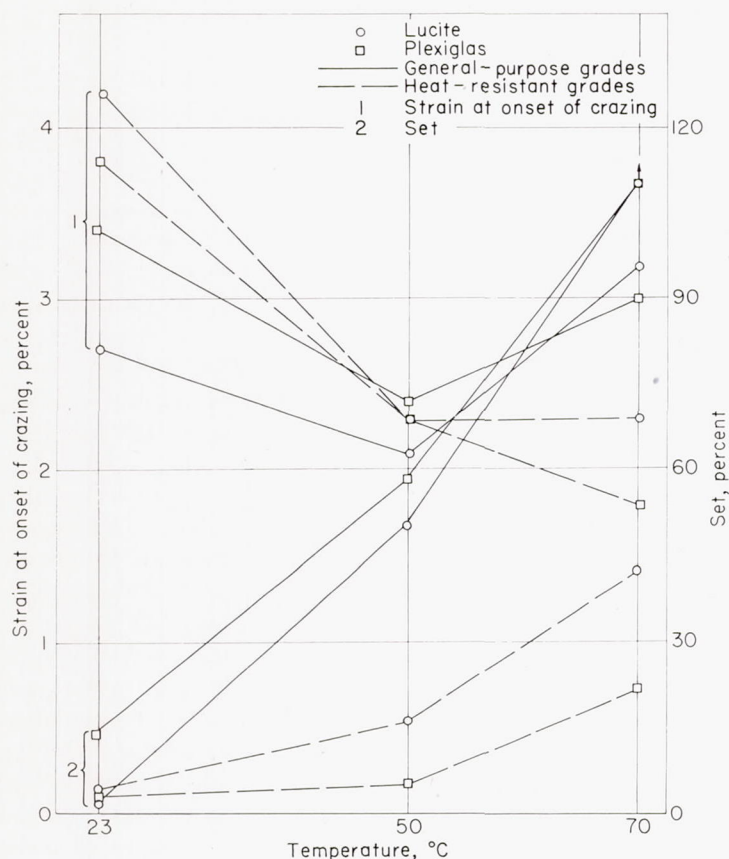


FIGURE 3.—Variation of strain at onset of crazing and permanent set with temperature for acrylic plastics.

removed the testing speed was increased to about 0.6 inch per minute.

The average values of tensile strength and of stress at the onset of crazing for the four materials tested are shown graphically in figure 1, the secant modulus values, in figure 2, and the values of the strain at the onset of crazing and set, in figure 3.

Polymethyl methacrylate did not begin to craze at the same strain for all temperatures; in general, the strain decreased with increase in temperature. For three of the four samples tested the strain at crazing was statistically significantly lower at 50° C, when the samples were still well below the glass transition point, than it was at 23° C. No consistent trend is evident between 50° and 70° C.

The ratio of stress at the threshold of crazing to the maximum stress was, in general, between 80 and 95 percent for all the samples tested at 23°, 50°, and 70° C.

The tensile strength and secant modulus of elasticity decrease approximately linearly with increase in temperature. The strengths at 70° C of the general-purpose and heat-resistant grades of polymethyl methacrylate were reduced to about 30 and 50 percent, respectively, of the strengths at 23° C. The modulus values at 70° C were correspondingly reduced to about 40 and 70 percent of the values at 23° C.

#### EFFECT OF MOLECULAR WEIGHT ON CRAZING OF POLYMETHYL METHACRYLATE

Tensile and crazing properties were determined for five cast polymethyl methacrylate sheets in which the viscosity-

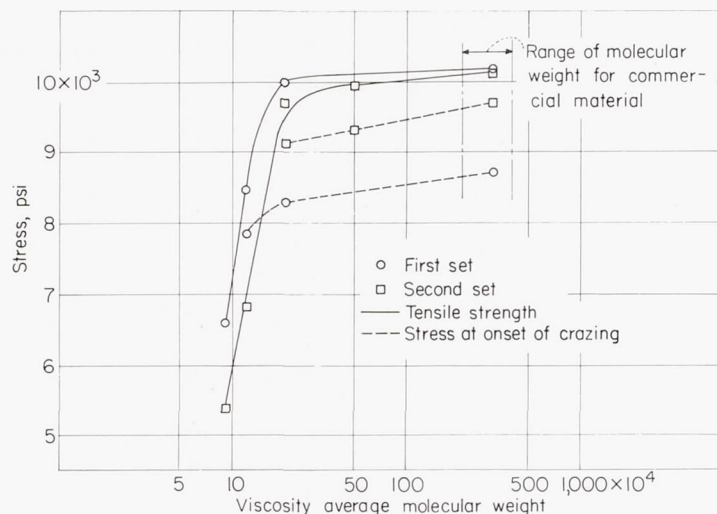


FIGURE 4.—Variation of tensile strength and stress at onset of crazing with molecular weight.

average molecular weights of the resin were 90,000, 120,000, 200,000, 490,000, and 3,160,000, respectively (ref. 3). Both stress crazing and stress-solvent crazing tests were conducted by the methods described in appendix A. The results are shown in figures 4 and 5. In the first set of stress-solvent crazing tests the solvent was applied by the blotter method with benzene as the solvent. In the second set of tests, both the brush and blotter methods were used with both benzene and isopropanol as solvents. For a given molecular weight, no significant differences in threshold values were observed among the various methods used in the second set of tests.

It was found that the tensile strength and strain at failure increase rapidly with increasing molecular weight at the lower molecular weights and begin to level off at molecular weights of approximately 200,000 and 500,000, respectively. There was no change in the modulus of elasticity over the range of molecular weights studied. The specimens with molecular weights of 90,000 and 120,000 broke at low strains without crazing. For the higher molecular weights, the stress and the strain at which crazing occurred increased with increasing molecular weights. In the stress-solvent

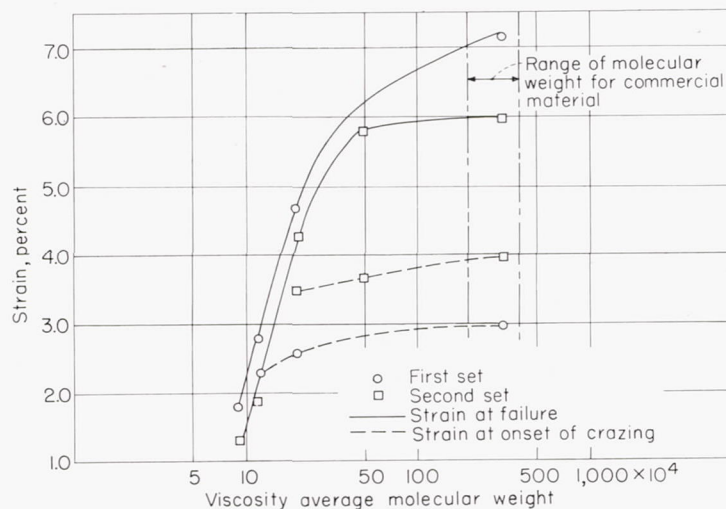


FIGURE 5.—Variation of strain at failure and strain at onset of crazing with molecular weight.



crazing tests, the materials with the three lowest molecular weights broke immediately upon crazing, usually at an observed craze crack. For the materials with the two highest molecular weights the craze resistance increased slightly with increase in molecular weight.

#### EFFECTS OF MULTIAXIAL STRETCHING ON CRAZING AND OTHER PROPERTIES OF TRANSPARENT PLASTICS

Improvement in the resistance of transparent plastics to crazing was sought by multiaxial stretch forming. The initial tests were conducted with general-purpose and heat-resistant grades of polymethyl methacrylate stretched 50 percent (ref. 4). A marked increase in the strain at the onset of crazing was noted in the standard short-time tensile test; in fact, most of the stretched specimens tested showed no crazing. The threshold stress for stress-solvent crazing with benzene applied by brush increased 70 to 80 percent. In long-time tensile tests (7 days), the threshold stress for stress crazing increased 40 to 50 percent. The tensile strength was unaffected, but the strain at failure was increased from 10 percent to about 60 percent. This considerable increase in strain at failure suggested that enclosures made from multiaxially stretched acrylic sheets might have not only greatly improved crazing resistance but also sufficient toughness and resistance to gunfire to obviate the need for the use of the heavier laminated acrylic materials.

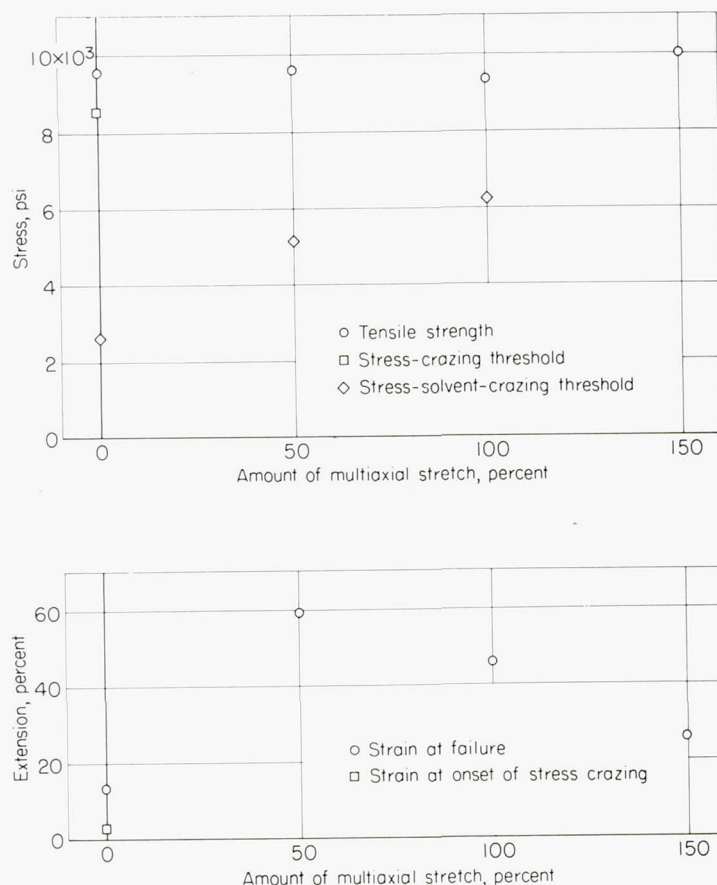


FIGURE 6.—Effect of multiaxial stretching on tensile properties of heat-resistant polymethyl methacrylate at 23° C. None of stretched specimens crazed in the stress-crazing test.

In view of these favorable results with polymethyl methacrylate stretched 50 percent, the effects of 100- and 150-percent multiaxial stretching were investigated (ref. 5). The tests were conducted with both general-purpose and heat-resistant grades of the acrylic plastic and the results are shown in figure 6. The tensile strength did not change for the 100-percent-stretched material but increased 6 to 12 percent for the 150-percent-stretched material. The strain at failure increased from approximately 7 percent for the unstretched material to 50 and 25 percent for the 100- and 150-percent-stretched materials, respectively. None of the stretched specimens crazed in the short-time tensile test. The threshold stress for stress-solvent crazing with benzene applied by blotter increased from approximately one-fourth of the strength for the unstretched material to approximately three-fourths for the 100-percent-stretched material. Most of the 150-percent-stretched specimens did not solvent craze even at tensile stresses very close to the ultimate strength. These observations indicate that the resistance to crazing increases markedly with increasing degrees of multiaxial stretching.

Tests were then conducted to determine the effects of multiaxial stretching on various properties of three heat-resistant transparent plastics, namely, polymethyl methacrylate (Lucite HC-222), modified polymethyl methacrylate (Plexiglas 55), and polymethyl alpha-chloroacrylate (Gafite and resin C). The properties measured for samples of these materials unstretched and multiaxially stretched approximately 50, 100, and 150 percent, depending upon the stretching limitations of the particular material, were as follows: Tensile strength including crazing threshold stress, strain at failure, secant modulus of elasticity, stress-solvent crazing with ethylene dichloride applied by blotter, dimensional stability at elevated temperatures, and resistance to abrasion. The method of stretching the samples and the testing procedures are described in appendixes A and B.

These tests, discussed in reference 6, showed that polymethyl methacrylate and polymethyl alpha-chloroacrylate can be multiaxially stretched at least 150 percent, whereas Plexiglas 55 (modified polymethyl methacrylate) cannot be stretched more than 85 percent with the apparatus used.

Multiaxial stretching causes the following general effects on the properties of the transparent plastics studied:

(1) Large increases in resistance to stress crazing and to stress-solvent crazing. This resistance increases with increasing degrees of stretching (table II).

(2) A slight increase in tensile strength (table II).

(3) A large increase in strain at failure (table II).

(4) Little effect on the tensile secant modulus of elasticity (table II).

(5) A decrease in the resistance to surface abrasion (table III).

Annealing increases the tensile strength of the stretched materials slightly and has the same effect for some of the unstretched materials. The resistance of both unstretched and stretched materials to stress-solvent crazing is usually increased markedly by annealing. However, the stress-crazing behavior of the unstretched materials is not affected



by annealing in most cases. Resistance of the stretched materials to surface abrasion is not affected by annealing.

As an alternative to the use of prestretched material to achieve improved craze resistance and toughness in acrylic enclosures, there is the possibility of preparing a more highly stretched enclosure directly, such as by forming a larger and more deeply drawn enclosure than required and then using only the central portion of the formed piece. Either method would improve the craze resistance, particularly at the rim, where there is likely to be stress concentration and where contact with solvents of adhesives used to seal the enclosure is quite likely; in a normally formed enclosure, the craze resistance is a minimum at the rim.

#### STRESS-STRAIN BEHAVIOR OF STRETCHED ACRYLICS

Typical stress-strain diagrams for unstretched and stretched heat-resistant polymethyl methacrylate and polymethyl alpha-chloroacrylate are presented in figures 7 and 8. The shape of the stress-strain curve of polymethyl methacrylate is not appreciably altered by the stretching, but that of polymethyl alpha-chloroacrylate is markedly affected. The unstretched polymethyl alpha-chloroacrylate failed before reaching a yield point; the stretched materials, however, show yield points.

In the tests conducted on stretched polymethyl methacrylate, very little increase in tensile strength was observed for the stretched materials over that of the unstretched. However, there was a marked decrease in the cross section of tensile specimens of the stretched material prior to failure at high strains, whereas the unstretched material broke at low strains with little change in cross section. Thus, the true stress at failure was probably much greater for the stretched specimens than that based on the original area.

For this reason, several tests were conducted on specimens of stretched heat-resistant polymethyl methacrylate without increasing the speed of testing when the strain reached 10 percent and the strain gage was removed. A speed of 0.05 inch per minute was used up to failure. Starting at

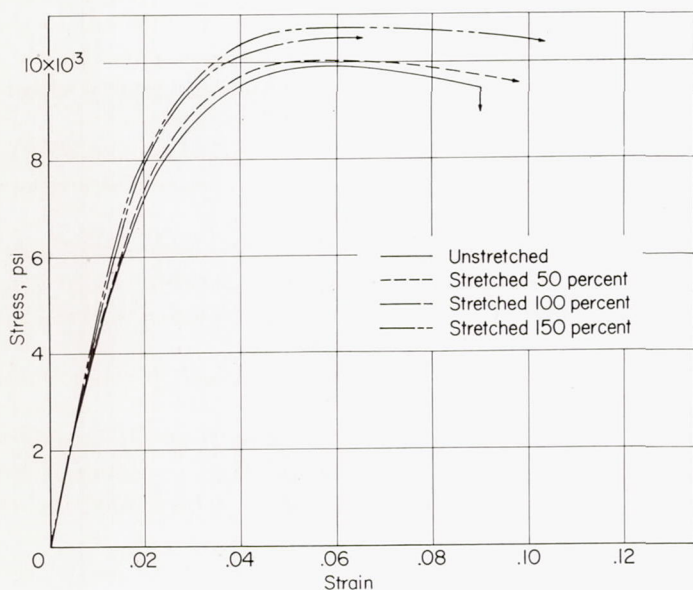


FIGURE 7.—Stress-strain diagrams of heat-resistant polymethyl methacrylate.

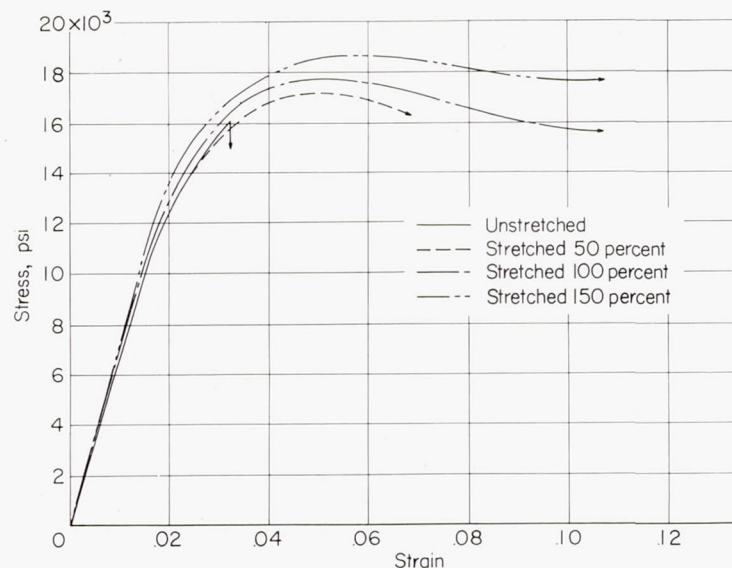


FIGURE 8.—Stress-strain diagrams of polymethyl alpha-chloroacrylate.

10-percent strain and continuing at intervals of 10-percent strain until failure, the width and thickness of the test specimens were measured with micrometer calipers to the nearest thousandth of an inch. The load was observed at each reading. From these data, the true stress at various strains could be calculated. Since most of the specimens of the stretched chloroacrylate materials broke at strains of 20 percent or less with little decrease in cross section, no measurements of this type were made on these specimens.

A typical true stress-strain diagram for the stretched polymethyl methacrylate is shown in figure 9. The results show that the true stress at the yield point is approximately 10 percent greater than the tensile strength because of the reduction in the cross-sectional area. The materials with the highest tensile strength did not have the highest true stress at failure. The 50-percent-stretched materials, which elongated the most and thus decreased the most in area, had the highest values for true stress at failure. That is, for each material, the true stress at failure was related to the strain at failure. The true stress at failure varied from approximately 25 to 50 percent greater than the tensile strength.

From the measurements made in the above tests of the changes in dimensions of the tensile specimens of the stretched

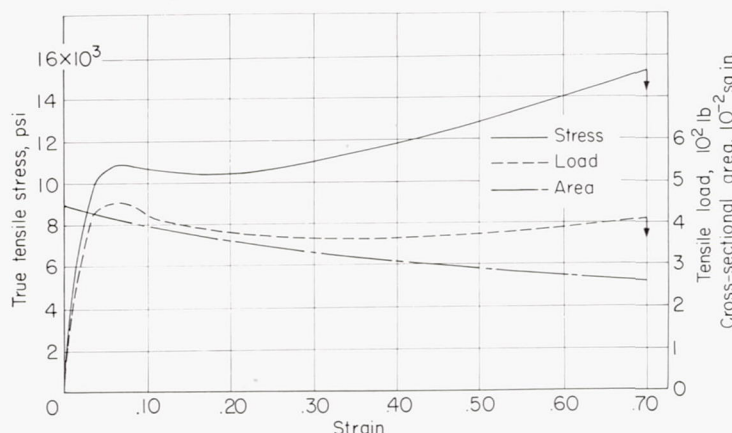


FIGURE 9.—Stress-strain diagram of heat-resistant polymethyl methacrylate multiaxially stretched 50 percent.



materials, it was possible to calculate values for Poisson's ratio. This is the ratio of lateral strain to axial strain. These values were calculated from changes in width and changes in thickness for each specimen, starting at 10 percent axial strain, at intervals of 10 percent strain to failure. The results show that Poisson's ratio is initially approximately 0.4 to 0.5 and decreases to approximately 0.3 to 0.4 as the strain increases. The reported value for Poisson's ratio for unstretched polymethyl methacrylate is 0.35.

#### RETENTION OF STRUCTURE ON HEATING OF STRETCHED ACRYLICS

The stretched materials will recover gradually if heated to a high enough temperature. The higher the heat-distortion point of the unstretched material, the lower is the extent of recovery of the stretched material at any given temperature within the range investigated. For any material, the higher the degree of stretching, the greater is the extent of recovery at a given temperature. Most of the recovery occurs in the first 2 hours (table IV).

The retention of the structure of stretched acrylic plastics when heated while restrained was also investigated by conducting stress-solvent crazing tests on tapered tensile specimens of heat-resistant polymethyl methacrylate that had been multiaxially stretched and then heated while restrained. Three disks were prepared at 50-percent, 100-percent, and 150-percent stretch. One disk at each degree of stretch was heated for 17 hours at 90° C, one for 6 hours at 115° C, and one for  $\frac{3}{4}$  hour at 130° C. The heating period at each temperature was determined experimentally as the maximum period that the formed pieces could be heated without tearing.

The results of these tests are presented in table V. The data indicate that heating while restrained does not affect the structure of multiaxially stretched acrylic plastic appreciably, as measured by crazing resistance.

In addition, the degree of stretch of each formed disk was observed by measuring the distance between points drawn on each sheet prior to forming. There was no significant change in these distances during the heating periods, indicating that the degree of stretching was not changing.

Thus, there is no apparent reorientation of the polymer chains if the stretched material is restrained while it is heated above the glass transition temperature for the times and temperatures investigated. From a practical point of view, this means that multiaxially stretched material can be heated for forming without a change in its structure or loss of orientation if it is restrained at the edges.

#### APPEARANCE OF CRAZED SPECIMENS

The patterns of crazing appearing on stress-crazed and stress-solvent-crazed specimens of polymethyl methacrylate are shown in figure 10. The stress crazing of polymethyl methacrylate is apparent in figure 11 as a rather uniform blushing of the surface, which is common for this material. The crazing of the modified polymethyl methacrylate, although not nearly so uniform nor so dense, also appeared on the surface only. The stress crazing of the polymethyl alpha-chloroacrylate specimens was rather uniform and

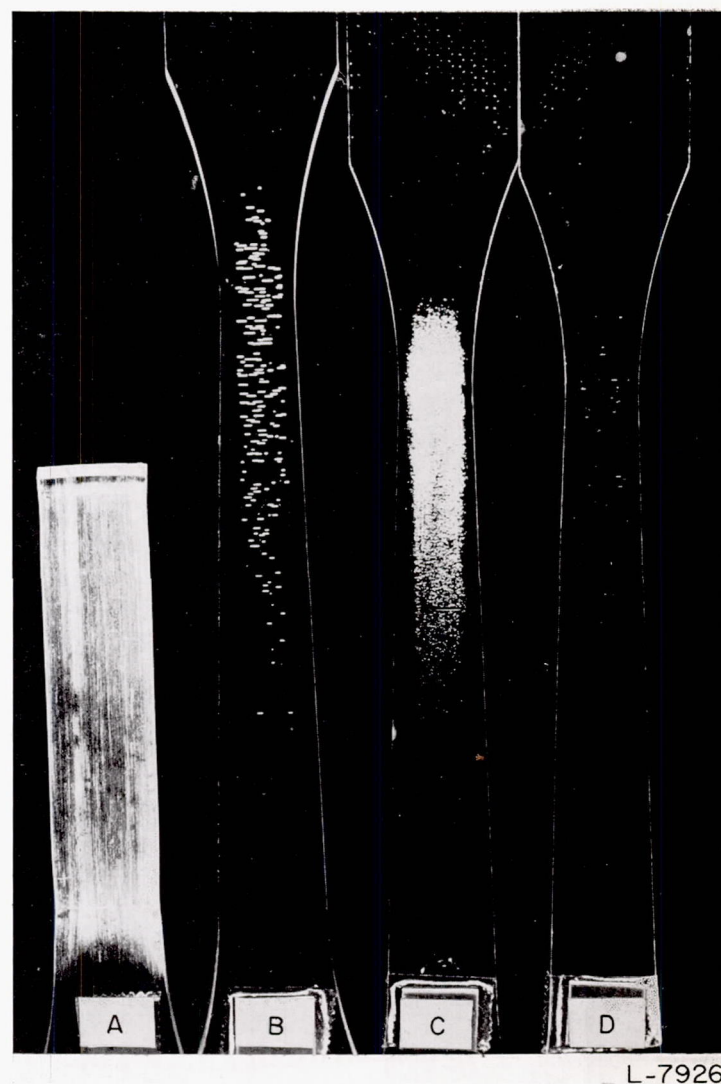


FIGURE 10.—Crazed tensile specimens of polymethyl methacrylate. A, unstretched, crazed during short-time tensile test; B, unstretched, stress-solvent crazed with benzene, maximum stress, 2,400 psi; C, multiaxially stretched 100 percent, stress-solvent crazed with benzene, maximum stress, 7,000 psi; and D, multiaxially stretched 150 percent, stress-solvent crazed with benzene, maximum stress, 10,000 psi.

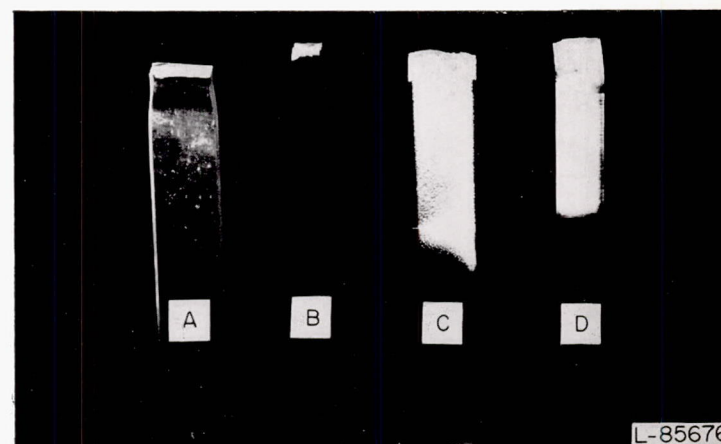


FIGURE 11.—Stress-crazed specimens of heat-resistant polymethyl methacrylate (A and B) and polymethyl alpha-chloroacrylate (C and D). Note internal crazing apparent in side view D of polymethyl alpha-chloroacrylate but not in side view B of polymethyl methacrylate.



quite dense and was apparent in the interior of the specimens as well as on the surface (fig. 11).

### FRACTURE BEHAVIOR

The fracture surfaces of the unstretched polymethyl methacrylate and modified polymethyl methacrylate specimens were flat and relatively smooth and were perpendicular to the cast faces. A smooth mirrorlike area was apparent on each fracture surface and was probably the point at which fracture initiated. The fracture surfaces of the polymethyl alpha-chloroacrylate specimens were very rough and uneven and usually slightly rounded. Numerous small pieces broke out of the fracture surfaces of the chloroacrylate specimens at failure. It was very difficult to detect a mirrorlike area on most of these specimens. Examples of the fracture surfaces are shown in figure 12.

The fracture surfaces of the stretched materials showed laminar structure. This structure is probably due to the orientation of the molecular chains in layers parallel to the plane of the sheet. The higher the degree of stretching, the more apparent was this layerlike orientation. The material thus tends to act as an assembly of independent laminae in resisting impact loads. The laminar structure of the stretched acrylic sheets also offers the possibility of obtaining resistance to shattering of pressurized acrylic canopies by shrapnel without the necessity of employing the heavier and more expensive acrylic laminate made with a safety-glass type of vinyl interlayer.

In many cases, a triangular-shaped piece split out of a tensile specimen of stretched material at the point of failure.

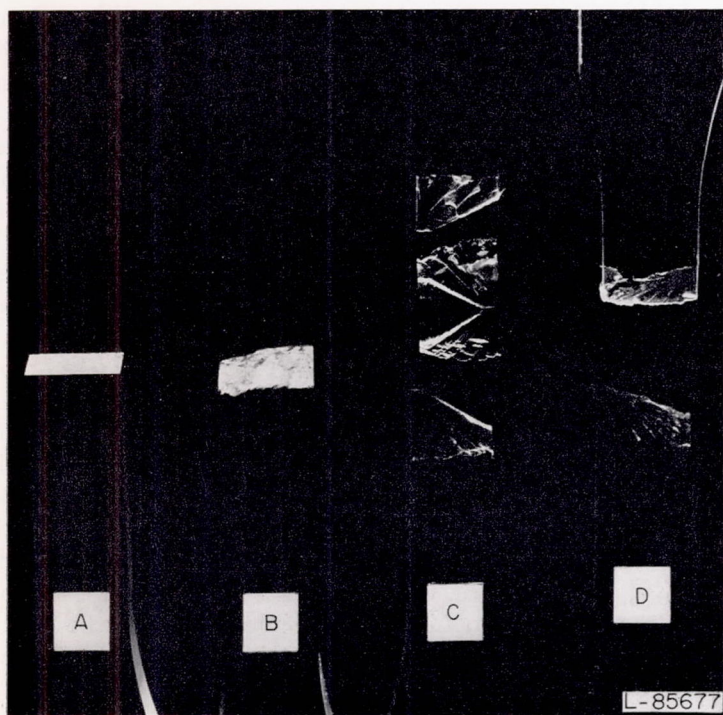


FIGURE 12.—Fracture surfaces of unstretched and multiaxially stretched acrylic plastics. A, unstretched polymethyl methacrylate; B, unstretched polymethyl alpha-chloroacrylate; C, modified polymethyl methacrylate stretched 45 percent; and D, polymethyl alpha-chloroacrylate stretched 100 percent. Note third piece broken out of specimen C (turned over). Specimen D broke into only two pieces (top piece is turned over).

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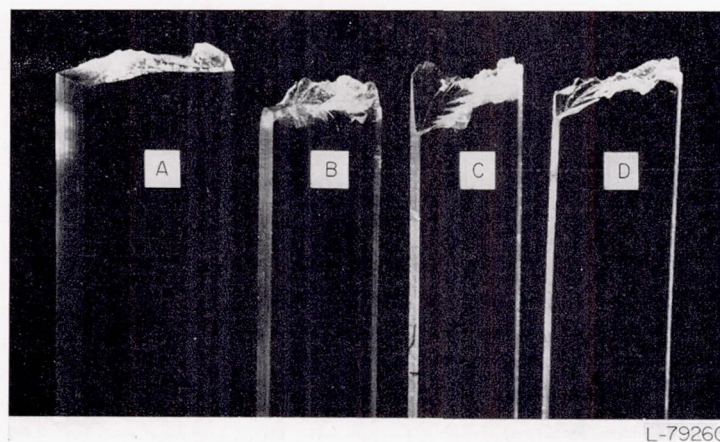


FIGURE 13.—Side view of fracture surfaces of polymethyl methacrylate, tensile specimens with varying degrees of multiaxial stretching. A, unstretched; B, stretched 50 percent; C, stretched 100 percent; and D, stretched 140 percent.

This phenomenon, shown in figure 12, probably represents a combination of tensile failure and shear failure. Further examples of the fracture behavior of multiaxially stretched polymethyl methacrylate are shown in figure 13.

### X-RAY DIFFRACTION PATTERNS

X-ray diffraction patterns were obtained on both stretched and unstretched polymethyl methacrylate, using a recording Geiger counter spectrometer with a copper target and nickel filter. The patterns were similar to those obtained by Krimm and Tobolsky (ref. 7), with halos at Bragg spacings of 6.5 and 3.0 Å for both the unstretched and the stretched materials, instead of 6.60 and 2.92 Å as reported by the above authors. They attributed the former spacing to inter-chain interferences and the latter, to intramolecular interferences. The height of the 6.5 Å peak was approximately 30 percent higher for the stretched material than for the unstretched. This would indicate increased orientation in the stretched polymer, which is expected from the nature of the stretching operation. There was a slight decrease noted in height of the 3.0 Å peak of the stretched samples, but it is questionable whether this change is significant.

### MECHANISM OF CRAZING

The following mechanism of crazing, somewhat similar to that proposed by Maxwell and Rahm (ref. 8), is postulated. The crazing is assumed to start at submicroscopic flaws or weak points. Such weak points may be submicroscopic regions in which by chance the polymer chain segments are oriented normal to the applied tensile stress. With sufficient stress a separation between portions of adjacent chains occurs; a stress concentration exists at the apex of the crack and the latter grows until it reaches a region in which the polymer chain segments are oriented approximately in the direction of the tensile stress. The crack either does not grow or grows slowly unless the tensile stress is greatly increased. Subsequent crack growth may involve rupture of primary valence bonds, especially if the stress is relatively high, of the order of the tensile strength.

In multiaxial stretching, the chain segments turn into a position more nearly parallel to the surface, and this angular change is dependent on the degree of stretching. The chain



segments do not, on the average, change the angle of their projections on the plane of the sheet with respect to the length or width of the sheet. Bailey (ref. 9) previously made similar statements for polymer chains. As the orientation increases, it may become more difficult for a submicroscopic crack to propagate through the thickness of the sheet because of the development of "cleavage" planes. It is then possible that, in highly formed polymethyl methacrylate, submicroscopic cracks form on the surface of a specimen when a tensile load is applied. The growth of cracks through the sheet is retarded by the planar orientation, however, and the specimen fails before the cracks become visible. In long-time tensile tests on polymethyl methacrylate stretched 50 percent, the crazing cracks, after becoming visible, grew more slowly as compared with those on the corresponding unstretched specimens.

The initiation of crazing may also be associated with residual stresses leading to local tensile failures, as postulated by Russell (ref. 10), or may occur at other types of flaws which would be points of localized stress concentration. These flaws might be inhomogeneities in chemical composition, such as residual catalyst, or physical surface defects resulting from the casting operation. The importance of flaws in effecting the fracture of other materials has been recognized. Griffith (ref. 11) has proposed a theory of the strength of glass based on the presence of surface cracks. The importance of structural inhomogeneities in the failure of metals has been reported by Epremian and Mehl (ref. 12). They found that inclusions play, by far, the dominant role in the fatigue behavior of metals. Multiaxial stretching probably would alleviate the effects of some types of submicroscopic flaws in cast acrylic sheet, since the material is heated to the rubbery state and then stretched. This would delay the formation of cracks in stretched material.

The orientation of the biaxially stretched material is apparent not only from the previously mentioned X-ray diffraction measurements but also from the laminar structure of the fracture surface of a stretched specimen, as compared with the amorphous appearance of an unstretched specimen (figs. 12 and 13). This change from an amorphous to a laminar structure could account for the increase in tensile strength noted for the material stretched 140 percent and more. When the degree of orientation is high enough, the material might act as an assembly of independent laminae parallel to the plane of the sheet, and the force required to rupture a series of such layers would be greater than that required to rupture a single layer of material of the same total thickness. The latter would be typical of the structure of unstretched material.

In regard to stress-solvent crazing, mechanisms have been suggested by various authors (refs. 10, 13, and 14) which while differing in some aspects include as a factor the concept of the solvent acting as a plasticizer. By using this concept the mechanism suggested above for stress crazing may be modified to include the influence of solvents as follows: The solvent molecules penetrating the surface of the polymer tend to surround portions of the polymer chains and reduce the forces required to separate them. Because of this weakening influence of the solvent molecules at a surface flaw such as a region of normal orientation of

the polymer chains, the stress concentration that can be withstood is reduced and a tiny crack develops at a lower applied stress than in the absence of solvent. The solvent molecules probably fill the crack by capillarity as it grows and continue to exert a weakening influence at the apex. In this connection it has been suggested by Hopkins, Baker, and Howard (ref. 14) that another weakening influence at the apex of a crack is the film-spreading pressure of the crazing liquid.

The effect of stretching on stress-solvent crazing might be expected to be similar to that for stress crazing. The reduction in the number and size of the regions of normal orientation and the increase in the regions of parallel orientation should result in higher threshold stresses for the stretched material. Also, for stretched material as for unstretched, the crazing stress should be lower in the presence of than in the absence of solvent owing to the weakening influence of the solvent.

The decrease in abrasion resistance of the stretched material may also be due to its laminar structure. The oriented chains that are essentially parallel to the surface may offer less resistance to abrasion than that offered by the randomly oriented chains of the unstretched material.

### CONCLUSIONS

Tests were conducted to determine the crazing behavior of various types of transparent plastics and the effect of multiaxial stretching of the plastics on their crazing resistance and various physical properties. The results and conclusions may be summarized as follows:

1. Moderate stress-solvent crazing of both general-purpose and heat-resistant grades of polymethyl methacrylate resulted in a loss of tensile strength of approximately 30 percent. This order of loss in strength was observed in the presence of either a few large craze cracks or more numerous fine cracks.
2. In stress-crazing tests at 23°, 50°, and 70° C with the same materials, the ratio of the stress at the threshold of crazing to the maximum stress was, in general, between 80 and 95 percent for all the samples.
3. The strain at which polymethyl methacrylate crazes shows, in general, a tendency to decrease with increase in temperature.
4. Polymethyl methacrylates with viscosity-average molecular weights of 90,000 and 120,000 broke at low strains without crazing; for samples having molecular weights of 200,000, 490,000 and 3,160,000, the stress and strain at which crazing occurred increased with increasing molecular weight.
5. In stress-solvent crazing tests, the materials with the three lowest molecular weights broke immediately upon crazing, usually at an observed craze crack. For the materials with the two highest molecular weights, the craze resistance increased slightly with increase in molecular weight.
6. Multiaxial stretching of polymethyl methacrylate had the following effects on crazing behavior and physical properties:
  - a. The specimens stretched 100 and 150 percent did not craze in the short-time tensile test.
  - b. The threshold stress for stress-solvent crazing with benzene increased from approximately one-fourth of the



tensile strength for the unstretched material to approximately three-fourths for the 100-percent-stretched material. Most of the 150-percent-stretched specimens did not solvent craze even at stresses very close to the tensile strength. These results indicate that the resistance to crazing increases markedly with increasing degree of multiaxial stretching.

c. The tensile strength and modulus of elasticity of the polymethyl methacrylates were affected only slightly by the multiaxial stretching.

d. The strain at failure of the polymethyl methacrylates was increased several fold (up to 60-percent strain) by multiaxial stretching, thus imparting toughness to the stretched sheets.

7. Multiaxial stretching of modified polymethyl methacrylate and polymethyl alpha-chloroacrylate gave comparable results.

8. Some decrease in the resistance to surface abrasion was observed when the materials were stretched multiaxially.

9. X-ray diffraction patterns and the laminar structure of the fracture surfaces of the stretched acrylic plastics indicated orientation of the molecular chains in layers parallel

to the plane of the sheet. The material thus tends to act as an assembly of independent laminae in resisting impact loads.

10. It is postulated that, in highly stretched acrylic sheets, the growth of submicroscopic surface cracks through the sheet is retarded by the planar orientation and the specimen fails before craze cracks become visible. Likewise, the stretched acrylic material is resistant to stress-solvent crazing because the weakening influence of either the solvent molecules or a crack caused by their presence is not readily transmitted through the layers of parallelly oriented polymer molecules.

11. The considerable increase in strain at failure suggested that enclosures made from multiaxially stretched acrylic sheets might have not only greatly improved crazing resistance but also sufficient toughness and resistance to gunfire to obviate the need for the use of the heavier laminated acrylic materials.

NATIONAL BUREAU OF STANDARDS

WASHINGTON, D. C., *December 28, 1955.*



## APPENDIX A

### METHODS OF TESTING

#### STANDARD TENSILE TESTS

The standard tensile tests were made in accordance with Method 1011 of reference 15 using the type 1 specimen. The tests were conducted on a 2,400-pound-capacity hydraulic universal testing machine. Load-extension data were recorded graphically using a Southwark-Peters extensometer and recorder. A testing speed of 0.05 inch per minute was used up to 10-percent strain; at this point the gage was removed and the speed increased to approximately 0.25 inch per minute. Strains greater than 10 percent were measured with dividers.

#### STRESS-SOLVENT CRAZING TESTS

The stress-solvent crazing tests were conducted at 23° C and 50-percent relative humidity on tensile specimens tapering in width from 0.500 to 0.333 inch over a 3-inch reduced section. Thus, for a given applied load the stress varied over the length of a specimen from a value  $S$  at the maximum cross section to  $1.5S$  at the minimum. Two methods of preparing and testing the specimens were used:

(1) Brush method. Solvent was applied to the specimen under load as follows: A controlled amount of solvent, 0.03 to 0.04 gram, was put on a No. 1 camel's hair brush (about 0.1 inch in diameter and 0.5 inch long) from a marked glass dropper. The central  $\frac{1}{4}$ - by 3-inch portion of the specimen was stroked with the brush until the latter was dry. The load was maintained for 4 minutes. The solvent-crazed specimens were examined under suitable lighting and the threshold of crazing noted.

(2) Blotter method. A predetermined load was applied to the specimen, and a solvent-saturated blotter, backed with a block of polyethylene for rigidity, was held against one face of the specimen for 10 seconds. The load was removed after 30 seconds, and the stress at the point at which crazing terminated was calculated as the threshold stress for stress-solvent crazing. For a given material, this stress will usually vary with the solvent used.

#### DIMENSIONAL-STABILITY TESTS

Dimensional-stability tests were conducted to provide thermal-recovery data and to provide data from which annealing conditions for the stretched materials could be determined. The specimens were small irregular pieces remaining after tensile and abrasion specimens were cut from the stretched disks and were approximately 1 inch by 2.5 inches

in size. Two lines approximately 1.5 inches apart were scribed on the surface of the specimens with a razor blade and the exact distance between the lines read to the nearest hundredth of an inch using a steel scale graduated in hundredths of an inch and a magnifying glass. The specimens were then laid on a sheet of plate glass and placed in an air-circulating oven at the test temperature. At the end of 2 hours, the specimens were removed from the oven and allowed to cool for 5 minutes, and the distance between the lines was measured. The specimens were then replaced in the oven and the readings repeated, in most cases, at the end of 6 hours, 1 day, 2 days, and 3 days. Several specimens were measured after they had cooled to room temperature, and no significant difference was found in the measurements made while the specimens were hot and those made after they had completely cooled. Four specimens of each degree of stretch of each material were tested at each temperature.

#### TESTS FOR ABRASION RESISTANCE

The resistance to abrasion was determined for unstretched and stretched materials, following Method 1092.1 of reference 15. A Taber abraser was used with CS-10 Calibrase wheels and a load of 1,000 grams on each wheel. Haze and light-transmission measurements were made in accordance with Method 3022 of reference 15, using an integrating-sphere haze meter. These measurements were made after 0, 10, 25, 50, 75, 100, 150, 200, and 250 revolutions of the abrader.

#### TESTS ON HEAT-TREATED AND ANNEALED SPECIMENS

Unstretched tensile specimens of each material were subjected to the same heating and rapid cooling cycle as that used in stretching to determine the effect of this cycle on the tensile properties. In addition, unheated and heated unstretched tensile specimens as well as stretched tensile specimens were annealed prior to testing. The annealing temperature for each material was selected from the results of the dimensional-stability tests and was the maximum temperature at which the stretched material could be heated for 6 hours with less than 5-percent relaxation. The temperatures selected were 90° C for the heat-resistant polymethyl methacrylate, 100° C for the modified polymethyl methacrylate, and 110° C for the polymethyl alpha-chloroacrylate. The specimens were allowed to cool slowly to room temperature in the oven after the heat and the fan were turned off.



## APPENDIX B

### STRETCHING PROCESS

#### EQUIPMENT AND PROCEDURE

A vacuum stretching apparatus which would produce flat multiaxially stretched disks about 10 inches in diameter was designed following suggestions offered by Mr. W. F. Bartoe of the Rohm & Haas Co., Inc. A schematic diagram of the stretching equipment is shown in figure 14 and a photograph, in figure 15. In this apparatus a sheet of acrylic material A, heated to the rubbery state, is clamped to the flange of the cylindrical forming vessel B. A partial vacuum is created in the vessel by connecting the latter to a vacuum system. The pressure differential, controlled by the plug valve C, draws the unclamped part of the sheet into the vessel. The form D, an open-end cylindrical tube a little smaller in diameter than the forming vessel and constrained by the guide E, is inserted into the vessel. The pressure differential is then removed quickly by admitting air through the plug valve F, so that the stretched acrylic sheet shrinks about the end of the form. The sheet cannot retract completely; the central portion remains uniformly stretched across the open end of the form. The stretched acrylic sheet, shaped like a top hat, is cooled to room temperature in the vessel before removal.

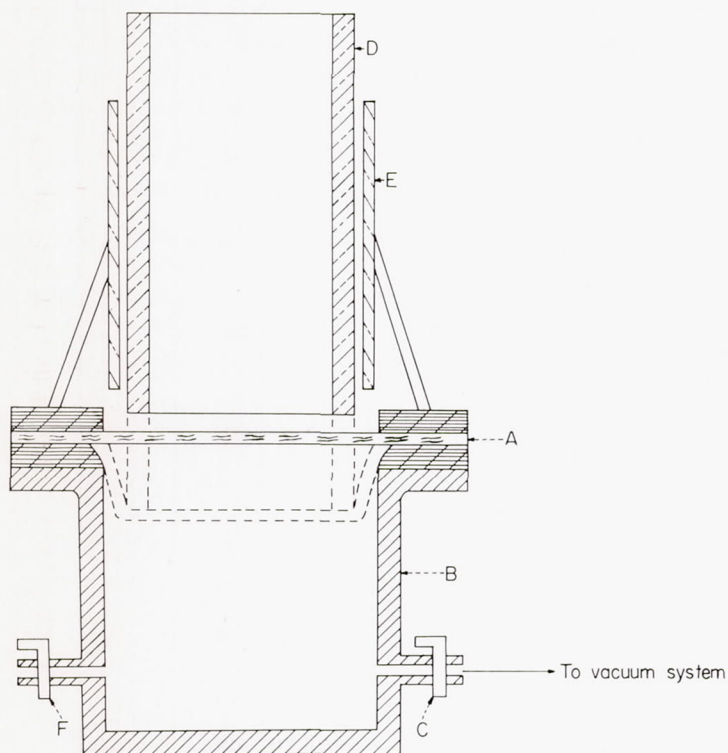


FIGURE 14.—Schematic drawing of vacuum stretching apparatus. A, plastic sheet to be stretched; B, forming vessel; C, valve to vacuum system; D, form; E, guide; and F, valve to atmosphere.

In practice, the stretching operation is done as quickly as possible so that the acrylic sheet will still be in the rubbery state when the pressure differential is removed; the time from removal of the sheet from the oven until stretching is complete is less than 1 minute.

#### UNIFORMITY OF STRETCHING AND EQUATION FOR ELONGATION

In order to determine whether the amount of stretching is uniform over the face of the multiaxially stretched pieces, the following experiments were made: A 10-inch disk of polymethyl methacrylate, which had been multiaxially stretched 150 percent after heating to 140° C, was marked off in 1-inch squares, then heated to 140° C, and allowed to assume its original size. The lines on the resulting disk were still equidistant within  $\pm 5$  percent. Since the standard deviation of the measurement and marking errors was



FIGURE 15.—Vacuum stretching apparatus partly disassembled after stretching a sheet of acrylic plastic. Stretched piece is on end of form which is held by operator.



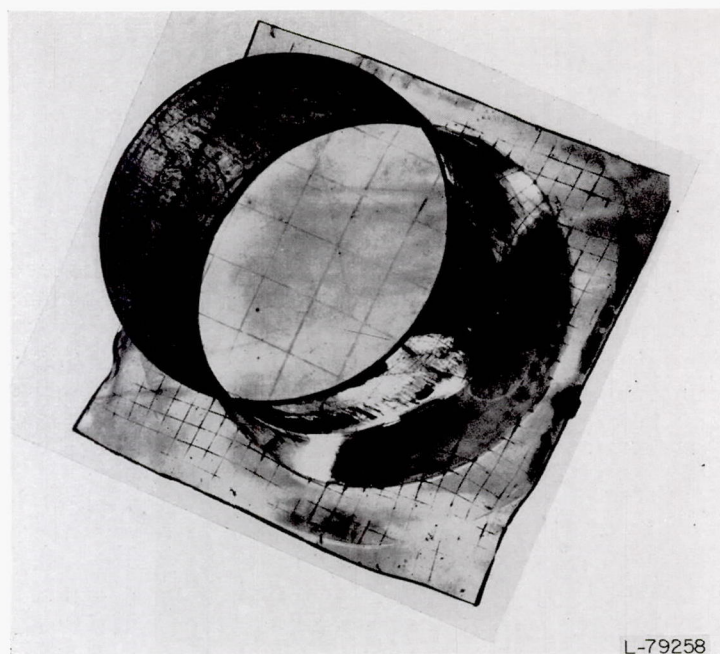


FIGURE 16.—Sample of stretched polymethyl methacrylate as removed from stretching apparatus. Large squares are on surface of flat top of hat-shaped piece.

also of this order of magnitude, this indicates that the amount of stretching was reasonably uniform over the face of the disk. Next, another piece of polymethyl methacrylate was marked with a square grid having a spacing of 15 millimeters; the piece was then multiaxially hot-stretched to an elongation of 150 percent. The lines on the flat top of the stretched plastic were still equidistant to within  $\pm 5$  percent, the experimental accuracy, verifying that the stretching was reasonably uniform (fig. 16). The length of the squares on the flat top when compared with the original length of the squares on the bottom rim indicates the degree of stretching. Test specimens are taken from the 10-inch-diameter flat top of the stretched piece.

The formula used for calculating the amount of multiaxial stretching in a stretched disk is

$$e = 100\sqrt{t_i/t_f} - 1 \quad (1)$$

where  $e$  is the elongation in percent and  $t_i$  and  $t_f$  are the initial and final thicknesses, respectively. This formula is based on the fact that the volume of the material remains essentially constant on stretching.

This property of the materials was verified by measuring the density of both 160-percent-stretched and unstretched materials. One sample of polymethyl methacrylate showed a decrease in density of 0.8 percent as a result of stretching to 160 percent strain. Three other samples of polymethyl methacrylate showed density changes of less than 0.2 percent as a result of this amount of stretching.

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TABLE I.—TENSILE STRENGTH OF STRESS-SOLVENT-CRAZED POLYMETHYL METHACRYLATE

[Specimens were taken from three sheets representing three production runs. Tests were made on standard tensile specimens of type I by Method 1011 of reference 15. Specimens were conditioned at least 3 weeks at 23° C and 50-percent relative humidity and tested 2 days after they were solvent crazed. Speed of testing was 0.05 in./min.]

| Material                  | Stress used<br>for crazing,<br>psi<br>(a) | Tensile strength of crazed<br>specimens |                                    | Average ten-<br>sile strength of<br>uncrazed con-<br>trol specimens,<br>psi<br>(a) (b) |
|---------------------------|---|---|------------------------------------|--|
|                           |   | Average,<br>psi                         | Percent of<br>control aver-<br>age |  |
| Treatment I <sup>e</sup>  |   |   |                                    |  |
| Lucite HC201_____         | 2, 000                                    | 5, 000                                  | 63                                 | 8, 000   |
| Lucite HC202_____         | 3, 000                                    | 6, 000                                  | 62                                 | 9, 700   |
| Plexiglas I-A_____        | 2, 400                                    | 4, 800                                  | 59                                 | 8, 100   |
| Plexiglas II_____         | 3, 000                                    | <sup>d</sup> 7, 600                     | 76                                 | 10, 000  |
| Treatment II <sup>e</sup> |   |   |                                    |  |
| Lucite HC201_____         | 3, 000                                    | <sup>f</sup> 6, 200                     | 78                                 | 7, 900   |
| Lucite HC202_____         | 4, 000                                    | 6, 900                                  | 71                                 | 9, 700   |
| Plexiglas I-A_____        | 3, 200                                    | 5, 400                                  | 67                                 | 8, 100   |
| Plexiglas II_____         | 4, 000                                    | 7, 800                                  | 76                                 | 10, 300  |

<sup>a</sup> Stress was maintained for 5 min. after benzene was applied. Control specimens were also subjected to this stress for 5 min.

<sup>b</sup> Control specimens were tested 2 days after they were loaded.

<sup>c</sup> Treatment I: No. 1 camel's hair brush (about 0.1-in. diameter, 0.5-in. length) was dipped in benzene and wiped against side of container so as not to drip. Then central ¼- by 2-in. portion of specimen was stroked twice with brush. This process was repeated nine times. Treatment I is designed to produce a few large crazing cracks. Each value is average of results for 12 specimens, unless otherwise noted.

<sup>d</sup> Average of results for 10 specimens.

<sup>e</sup> Treatment II: Benzene in amount of 0.03 to 0.04 g was put on No. 1 camel's hair brush. Then central ¼- by 2-in. portion of specimen was stroked repeatedly with brush. Treatment II is designed to produce numerous fine crazing cracks. Each value is average of results for 24 specimens, unless otherwise noted.

<sup>f</sup> Average of results for 23 specimens.



TABLE II.—EFFECT OF MULTIAXIAL STRETCHING ON TENSILE AND CRAZING PROPERTIES OF ACRYLIC PLASTICS

[Tests were conducted at 23° C and 50-percent relative humidity; each result is average of results for eight specimens unless otherwise noted]

| Degree of stretching, percent                   | Tensile strength, $\sigma_{max}$ , psi | Strain at failure, percent | Secant modulus, psi <sup>a</sup> | Stress and strain at onset of crazing |                   |                         | Solvent-crazing stress, psi <sup>b</sup> |
|---|--|----------------------------|----------------------------------|---------------------------------------|-------------------|-------------------------|--|
|   |  |                            |                                  | Stress, $\sigma_c$ , psi              | Strain, percent   | $\sigma_c/\sigma_{max}$ |  |
| Polymethyl methacrylate (Lucite HC-222)         |  |                            |                                  |                                       |                   |                         |  |
| 0   | <sup>c</sup> 9, 720                    | <sup>d</sup> 7. 4          | <sup>e</sup> $4. 6 \times 10^5$  | <sup>e</sup> 9, 070                   | <sup>e</sup> 3. 3 | 0. 93                   | <sup>e</sup> 910                         |
| 50  | 9, 730                                 | <sup>e</sup> 29            | <sup>f</sup> 4. 3                | ( <sup>h</sup> )                      | ( <sup>h</sup> )  | ( <sup>h</sup> )        | <sup>e</sup> 1, 680                      |
| 100   | 10, 100                                | <sup>e</sup> 37            | <sup>f</sup> 4. 7                | ( <sup>h</sup> )                      | ( <sup>h</sup> )  | ( <sup>h</sup> )        | <sup>e</sup> 2, 710                      |
| 150   | 10, 530                                | <sup>e</sup> 16            | <sup>f</sup> 5. 0                | ( <sup>h</sup> )                      | ( <sup>h</sup> )  | ( <sup>h</sup> )        | <sup>e</sup> 3, 910                      |
| Modified polymethyl methacrylate (Plexiglas 55) |  |                            |                                  |                                       |                   |                         |  |
| 0   | 10, 240                                | 6. 7                       | $4. 8 \times 10^5$               | 9, 580                                | 3. 4              | 0. 94                   | 2, 420                                   |
| 45  | 10, 660                                | <sup>g</sup> 42            | <sup>f</sup> 4. 8                | ( <sup>h</sup> )                      | ( <sup>h</sup> )  | ( <sup>h</sup> )        | 4, 060                                   |
| 85  | 10, 990                                | <sup>g</sup> 45            | <sup>f</sup> 5. 1                | ( <sup>h</sup> )                      | ( <sup>h</sup> )  | ( <sup>h</sup> )        | 5, 660                                   |
| Polymethyl alpha-chloroacrylate (Resin C)       |  |                            |                                  |                                       |                   |                         |  |
| 0   | 16, 170                                | 3. 1                       | $7. 4 \times 10^5$               | 13, 300                               | 2. 2              | 0. 82                   | 2, 850                                   |
| 50  | 17, 720                                | <sup>i</sup> 23            | <sup>i</sup> 7. 6                | ( <sup>h</sup> )                      | ( <sup>h</sup> )  | ( <sup>h</sup> )        | 6, 430                                   |
| 100   | 18, 310                                | <sup>i</sup> 12            | <sup>i</sup> 8. 2                | ( <sup>h</sup> )                      | ( <sup>h</sup> )  | ( <sup>h</sup> )        | 12, 950                                  |
| 150   | 18, 510                                | <sup>i</sup> 9             | <sup>i</sup> 8. 0                | ( <sup>h</sup> )                      | ( <sup>h</sup> )  | ( <sup>h</sup> )        | >18, 140                                 |

<sup>a</sup> Secant modulus of elasticity was calculated for stress range of 0 to 2,500 psi.<sup>b</sup> Solvent-crazing stress is minimum stress required to cause crazing upon application of ethylene dichloride.<sup>c</sup> Average of results for five specimens.<sup>d</sup> Average of results for three specimens.<sup>e</sup> Average of results for seven specimens.<sup>f</sup> Average of results for four specimens.<sup>g</sup> Average of results for six specimens.<sup>h</sup> Did not craze.<sup>i</sup> Average of results for two specimens.



TABLE III.—EFFECT OF MULTIAXIAL STRETCHING ON SURFACE ABRASION OF ACRYLIC PLASTICS AT 23° C

| Material                         | Degree of stretching, percent | Light transmission, percent <sup>(a)</sup> |                         | Haze, percent <sup>(a)</sup> |                         | Initial slope of abrasion curve, percent haze<br>number of revolutions |
|----------------------------------|-------------------------------|--|-------------------------|------------------------------|-------------------------|--|
|                                  |                               | Original                                   | Final                   | Original                     | Final                   |  |
| Lucite HC-222 <sup>b</sup> ----- | 0                             | 92.1 ± 0.1                                 | 88.4 ± 0.2              | 0.3 ± 0.1                    | 24.7 ± 0.6              | 0.21   |
|                                  | 50                            | 92.0 ± 0.1                                 | 87.6 ± 0.2              | .4 ± 0.1                     | 30.4 ± 0.7              | .38  |
|                                  | 100                           | <sup>c</sup> 91.9 ± 0.1                    | <sup>c</sup> 87.2 ± 0.2 | <sup>c</sup> .5 ± 0.1        | <sup>c</sup> 30.6 ± 1.0 | .43  |
|                                  | 150                           | 91.8 ± 0.2                                 | 86.8 ± 0.2              | .4 ± 0.1                     | 32.0 ± 1.3              | .45  |
| Plexiglas 55 <sup>b</sup> -----  | 0                             | 91.4 ± 0.1                                 | 88.1 ± 0.1              | .5 ± 0.1                     | 21.8 ± 0.3              | .19  |
|                                  | 45                            | <sup>c</sup> 91.7 ± 0.1                    | <sup>c</sup> 88.0 ± 0.2 | <sup>c</sup> .6 ± 0.1        | <sup>c</sup> 25.1 ± 0.6 | .26  |
|                                  | 85                            | 91.5 ± 0.1                                 | 87.7 ± 0.1              | .6 ± 0.1                     | 26.6 ± 0.4              | .33  |
| Gafite <sup>d</sup> -----        | 0                             | 90.0 ± 0.2                                 | 87.5 ± 0.3              | .4 ± 0.1                     | 21.6 ± 0.7              | .17  |
|                                  | 50                            | 90.6 ± 0.1                                 | 86.8 ± 0.2              | .6 ± 0.2                     | 25.4 ± 0.6              | .33  |
|                                  | 100                           | 90.5 ± 0.2                                 | 87.4 ± 0.2              | .2 ± 0.1                     | 23.8 ± 0.8              | .31  |
|                                  | 150                           | <sup>e</sup> 90.6 ± 0.3                    | <sup>e</sup> 86.8 ± 2.8 | <sup>e</sup> .2 ± 0.0        | <sup>e</sup> 25.2 ± 1.2 | .30  |
| Resin C <sup>d</sup> -----       | 0                             | 91.0 ± 0.2                                 | 87.9 ± 0.1              | .7 ± 0.1                     | 19.4 ± 0.4              | .14  |
|                                  | 50                            | <sup>e</sup> 90.9 ± 0.1                    | <sup>e</sup> 87.6 ± 0.2 | <sup>e</sup> .2 ± 0.1        | <sup>e</sup> 24.2 ± 0.4 | .26  |
|                                  | 100                           | 91.3 ± 0.1                                 | 87.0 ± 0.2              | .2 ± 0.1                     | 26.9 ± 1.0              | .30  |
|                                  | 150                           | <sup>e</sup> 90.3 ± 0.4                    | <sup>e</sup> 87.1 ± 0.1 | <sup>e</sup> .6 ± 0.1        | <sup>e</sup> 28.2 ± 2.1 | .30  |

<sup>a</sup> Final measurements were made after 250 revolutions.<sup>b</sup> Average of results for 12 specimens unless otherwise noted, plus or minus standard error.<sup>c</sup> Average of results for 11 specimens.<sup>d</sup> Average of results for six specimens unless otherwise noted, plus or minus standard error.<sup>e</sup> Average of results for five specimens.



TABLE IV.—DIMENSIONAL STABILITY OF MULTIAXIALLY STRETCHED ACRYLIC PLASTICS AT ELEVATED TEMPERATURES

[Each result is the average of results for four specimens]

(a) Polymethyl methacrylate (Lucite HC-222)

| Temperature,<br>°C | Time,<br>hr                    | Multiaxial stretch, percent |      |      |      |
|--------------------|--------------------------------|-----------------------------|------|------|------|
|                    |                                | 0                           | 50   | 100  | 150  |
| 80                 | Decrease in length, percent    |                             |      |      |      |
|                    | 2                              | 0                           | 0.1  | 0.5  | 0.8  |
|                    | 6                              | 0                           | .1   | .4   | .9   |
|                    | 24                             | 0                           | .2   | .7   | 1.1  |
|                    | 72                             | 0                           | .2   | 1.0  | 1.1  |
| 90                 | 2                              | 0                           | 1.2  | 1.9  | 2.5  |
|                    | 6                              | 0                           | 1.3  | 1.9  | 2.6  |
|                    | 24                             | 0                           | 1.6  | 2.4  | 3.0  |
|                    | 72                             | 0                           | 1.5  | 2.6  | 3.5  |
| 100                | 2                              | 0                           | 8.8  | 15.6 | 17.5 |
|                    | 6                              | 0                           | 12.1 | 19.1 | 20.2 |
|                    | 24                             | 0                           | 15.0 | 22.9 | 25.7 |
|                    | 48                             | 0                           | 15.8 | 24.2 | 28.0 |
|                    | 72                             | 0                           | 16.1 | 24.6 | 28.6 |
|                    | 144                            | 0                           | 16.4 | 25.3 | 29.7 |
|                    | Average initial thickness, in. |                             |      |      |      |
|                    |                                | 0.26                        | 0.10 | 0.06 | 0.04 |

(b) Modified polymethyl methacrylate (Plexiglas 55)

| Temperature,<br>°C | Time,<br>hr                    | Multiaxial stretch, percent |      |      |
|--------------------|--------------------------------|-----------------------------|------|------|
|                    |                                | 0                           | 45   | 85   |
| 90                 | Decrease in length, percent    |                             |      |      |
|                    | 2                              | 0                           | 0.4  | 0.8  |
|                    | 6                              | 0                           | .6   | 1.0  |
|                    | 24                             | 0                           | .8   | 1.0  |
|                    | 48                             | .1                          | 1.0  | 1.1  |
|                    | 72                             | .1                          | .9   | 1.1  |
| 100                | 2                              | 0                           | 1.4  | 1.6  |
|                    | 6                              | 0                           | 1.3  | 1.9  |
|                    | 24                             | .2                          | 1.5  | 2.1  |
|                    | 48                             | .2                          | 1.5  | 1.9  |
|                    | 72                             | .2                          | 1.5  | 2.1  |
| 110                | 2                              | 0                           | 10.2 | 13.0 |
|                    | 6                              | 0                           | 11.7 | 14.4 |
|                    | 24                             | .2                          | 13.4 | 15.4 |
|                    | 48                             | .3                          | 13.5 | 15.8 |
|                    | 72                             | .3                          | 13.9 | 16.1 |
|                    | Average initial thickness, in. |                             |      |      |
|                    |                                | 0.25                        | 0.12 | 0.07 |

TABLE IV.—DIMENSIONAL STABILITY OF MULTIAXIALLY STRETCHED ACRYLIC PLASTICS AT ELEVATED TEMPERATURES—Concluded

(c) Polymethyl alpha-chloroacrylate (Resin C)

| Temperature,<br>°C | Time,<br>hr                    | Multiaxial stretch, percent |      |      |      |
|--------------------|--------------------------------|-----------------------------|------|------|------|
|                    |                                | 0                           | 50   | 100  | 150  |
| 110                | Decrease in length, percent    |                             |      |      |      |
|                    | 2                              | 0.1                         | 0.4  | 1.0  | 1.1  |
|                    | 6                              | 0                           | .4   | .8   | .9   |
|                    | 24                             | 0                           | .8   | .9   | 1.2  |
|                    | 48                             | 0                           | .6   | .9   | 1.2  |
|                    | 72                             | .1                          | .9   | 1.1  | 1.3  |
| 120                | 2                              | .2                          | 2.0  | 3.2  | 4.1  |
|                    | 6                              | .1                          | 2.6  | 3.6  | 4.1  |
|                    | 24                             | .1                          | 2.7  | 3.7  | 4.4  |
|                    | 48                             | .1                          | 3.0  | 4.2  | 4.6  |
|                    | 72                             | .4                          | 3.4  | 4.2  | 5.0  |
| 130                | 2                              | 1.4                         | 32.2 | 45.0 | 51.5 |
|                    | 6                              | 1.4                         | 34.3 | 47.8 | 55.5 |
|                    | 24                             | 1.9                         | 35.8 | 49.5 | 58.8 |
|                    | 48                             | 1.6                         | 35.9 | 50.4 | 59.1 |
|                    | 72                             | 2.2                         | 36.2 | 50.8 | 59.7 |
|                    | Average initial thickness, in. |                             |      |      |      |
|                    |                                | 0.27                        | 0.10 | 0.06 | 0.04 |

TABLE V.—EFFECT OF HEATING WHILE RESTRAINED ON CRAZING BEHAVIOR OF MULTIAXIALLY STRETCHED HEAT-RESISTANT POLYMETHYL METHACRYLATE

| Percent stretch | Heating conditions |          | Stress-solvent crazing threshold, psi <sup>(a)</sup> | Standard error, psi |
|-----------------|--------------------|----------|--|---------------------|
|                 | Temperature, °C    | Time, hr |  |                     |
| 50              | Unheated           |          | 1,500  | 40                  |
|                 | 90                 | 17       | 1,210  | 40                  |
|                 | 115                | 6        | 1,270  | 80                  |
|                 | 130                | ¾        | 1,480  | 50                  |
| 100             | Unheated           |          | 2,170  | 40                  |
|                 | 90                 | 17       | 2,160  | 80                  |
|                 | 115                | 6        | 2,060  | 50                  |
|                 | 130                | ¾        | 2,720  | 70                  |
| 150             | Unheated           |          | 5,420  | 240                 |
|                 | 90                 | 17       | 5,420  | 20                  |
|                 | 115                | 6        | 4,200  | 40                  |
|                 | 130                | ¾        | 5,420  | 150                 |

<sup>a</sup> Ethylene dichloride was used as solvent for these crazing tests. Each result is average of results for five specimens.